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LOGAN WALLER PAGE, DIRECTOR.

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NAPHTHALENE IN ROAD TARS.

I.—THE EFFECT OF NAPHTHALENE UPON THE CONSISTENCY OF REFINED TARS.

BY

PRÉVOST HUBBARD,
Chemist, Office of Public Roads,

AND

CLIFTON N. DRAPER,
Assistant Chemist, Office of Public Roads.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Office of Public Roads,
Washington, D. C., August 2, 1911.

Sir: I have the honor to transmit herewith the manuscript of a circular, by Mr. Prévost Hubbard and Mr. Clifton N. Draper, of this office, on the Effect of Naphthalene upon the Consistency of Refined Tars. This publication is one of a series of papers which will be prepared under the general subject, Naphthalene in Road Tars. A systematic investigation of the effect of various constituents upon the quality and adaptability of tars used as road binders would seem to be of the greatest importance, first, because of the present lack of data bearing upon this subject, and second, because the utilization of tars in road treatment and construction seems destined to effect a large proportion of the road work in this country. I therefore respectfully request that this paper be issued as Circular 96 of this office.

Respectfully,

Logan Waller Page,
Director.

Hon. James Wilson,
Secretary of Agriculture.

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THE EFFECT OF NAPHTHALENE UPON THE CONSISTENCY OF REFINED TARS.

Naphthalene, $C_{10}H_8$, often occurs in coal tar in larger quantities than any other one hydrocarbon and for this reason it is natural to suppose that it exerts an appreciable influence upon the quality and applicability of coal tars used as road binders. In this country the use of tars in road treatment and construction has advanced rapidly during the past few years and upon the market to-day are to be found a number of tar preparations intended for such use. These preparations are as a rule made by distilling off the lighter and more volatile constituents from both crude coal tar and crude water-gas tar or mixtures of the two. The residual products, which vary in consistency according to the extent and method of distillation, are sold for road purposes. Many successes and many failures have resulted from the use of coal tar and water-gas tar road binders, and often no clew has been obtainable as to the reason for such diverse results. In view of this fact, a systematic study of the principal chemical constituents of road-tar preparations and their effect upon the quality of such preparations is now being made in the laboratories of the Office of Public Roads, United States Department of Agriculture.

In the present paper, which is the first of a series upon naphthalene, no attempt will be made to review the chemistry of this substance, since this discussion is reserved for a later publication which will cover the entire subject as presented in the individual papers. A few remarks concerning certain physical properties of naphthalene may, however, not be amiss at this point.

Naphthalene, in the pure state, exists in white crystalline masses of thin rhomboidal scales melting at 79° C. and having a boiling point of 218° C. Its specific gravity at 15° C. is 1.1517. It has a very characteristic odor, commonly familiar in moth balls, and is extremely volatile, considering its high molecular weight, so much so that in the manufacture of coal gas it is only partially deposited in the condensers, while the remainder is carried into the purifiers

and into the gas mains, where it deposits in the bends of pipes during cold weather and often causes them to become clogged. Naphthalene volatilizes far below its boiling point and, in crude tars, distills to a considerable extent with aqueous vapor and also with the light tar oils, which accounts for its occurrence in the first fractions. Even at ordinary temperatures, it volatilizes slowly and gives off a penetrating tarry odor. It is slightly soluble in hot water, but dissolves easily in alcohol, ether, fatty and essential oils, acetic acid, and especially in the phenols and lighter tar distillates. No entirely satisfactory method for the quantitative determination of naphthalene in tar has, as far as the authors are aware, been devised up to the present time, although methods have been put forth by various investigators for the determination of naphthalene in illuminating gas.

It is a rather generally accepted theory that, in the manufacture of coal gas, the formation of naphthalene is due to certain complex reactions which take place only at the high temperatures at which the retort is maintained in modern gas-house practice. According to Cooper,[1] "A few years ago—when lower temperatures were in vogue, and when lower makes per ton of coal carbonized were registered—naphthalene was an almost unknown quantity; but now that the stress of competition demands the highest possible output of gas, it seems also to bring in its train the formation of large quantities of naphthalene." It is certain, however, that other factors, such as the size, shape, and inclination of the retort with relation to the volume of the charge of coal, and the varying conditions to which the evolved gases are subjected before and during their passage from the retort, have a great deal to do with the quantity of naphthalene formed.

Tars used as road binders are for the most part soft pitches obtained by distilling from 15 to 30 per cent of the lighter products from the crude material. The soft pitch contains a large proportion of the naphthalene which may have been present in the original tar, and it is the study of the effect of naphthalene upon this grade of material that is the subject of this paper. As consistency is one of the most important properties of a road tar, it was thought well first to investigate the effect of varying percentages of naphthalene upon a given tar.

From its very nature naphthalene itself can not be considered as a binding material. For some time past it has been known, however, to serve as a flux for the binding constituents of tars, in spite of the fact that it is a crystalline solid. Thus it is possible to combine, by heating together, a hard tar pitch and a quantity of naphthalene with the formation of a soft product. It was thought, therefore, that

[1] Journal of Gas Lighting, Vol. CX, May 24, 1910, p. 498.

a comparison of its fluxing value with that of certain less volatile tar distillates would prove most instructive. For this purpose a representative coal tar was taken and distilled to 238° C. in order to remove all the naphthalene. This naphthalene-free tar pitch, which was used for the following tests, was so hard that it was difficult to make an impression on it with the finger. An arbitrary measure of the consistency of this pitch was then obtained by means of the New York Testing Laboratory float-test apparatus, which is customarily used for this purpose in the routine examination of tar products in the Office of Public Roads.[1]

The float apparatus, briefly described, consists of an aluminum float or cup, 3½ inches in diameter, into which is screwed a small brass conical collar or mold. This collar is ⅝ inch high, with an internal diameter at the top of ⅜ inch and at the bottom of ½ inch.

In making the test the brass collar is placed with the small end down on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chlorid nitrate and then with mercury. A small quantity of the material to be tested is heated in a metal spoon until quite fluid, with care that it suffers no appreciable loss by volatilization and that it is kept free from air bubbles. It is then poured into the collar in a thin stream until slightly more than level with the top. The surplus may be removed after the material has cooled to room temperature, by means of a spatula blade which has been slightly heated. The collar and plate are then placed in a tin cup containing ice water maintained at 5° C. and left in this bath for at least 15 minutes. Meanwhile another cup is filled about three-fourths full of water, placed on a tripod, and the water heated to any temperature at which it is desired to make the test. This temperature is accurately maintained, and is at no time throughout the entire test allowed to vary more than one-half a degree centigrade from the temperature selected. After the material to be tested has been kept in the ice water for at least 15 minutes, the collar and contents are removed from the plate and screwed into the aluminum float, which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid it is gradually forced upward and out of the collar until water gains entrance to the float and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the bitumen is determined by means of a stop watch and is taken as a measure of the consistency of the material under examination. Results so expressed are only relative, but they are comparable to within a good degree of precision. The temperature at which the water bath is maintained is purely an arbitrary matter and, for routine work in the office, 32° C.

[1] Bulletin 38, U. S. Dept. of Agriculture, Office of Public Roads, pp. 14–16.

and 50° C. have been selected as a matter of convenience when testing the comparatively soft and comparatively hard road tars.

For the work described in this circular 55° C. and 80° C. were adopted as most convenient temperatures. The former was selected after making a series of float tests upon the prepared coal tar pitch at temperatures varying from 40° C. to 60° C. In these tests it was found that at 40° C. and 45° C. the tar had not softened sufficiently to complete the test at the end of 1 hour; at 50° C. a test of 24 minutes and 18 seconds was obtained; at 55° C., 9 minutes and 47 seconds, and at 60° C., 3 minutes and 45 seconds. The duration of the test at 55° C. seemed most satisfactory as allowing sufficient leeway for comparative results without consuming too much time. It was decided to select 80° C. as a second working temperature, as it was the nearest convenient one to the melting point of naphthalene. It was thought that, by making consistency tests upon the naphthalene tar-pitch mixtures, later described, at both 55° C. and 80° C., the results would show not only how much the mixtures softened at the higher temperature, but what differences, if any, might be due to naphthalene below and above its melting point.

When the matter of temperatures had been decided upon and the consistency of the tar pitch had been determined at these temperatures, naphthalene mixtures were made as follows: Approximately 30-gram samples were accurately weighed into a series of small tin dishes, and varying percentages of c. p. flake naphthalene were added, starting with 0.5 per cent of naphthalene and gradually increasing this amount to the extent of 30 per cent. In all, 13 samples were prepared. Before adding the naphthalene, each weighed sample of tar was warmed in the tin dish until fairly fluid, after which the naphthalene was added and the mixture well stirred. It was found better to add the naphthalene a little at a time during the process of mixing rather than to add the entire amount at one time, as by so doing there was less danger of losing some of the naphthalene by volatilization and a uniform mixture was more readily obtained. As the naphthalene was added, an increase in the fluidity of the mixtures was readily seen. Where 20 per cent of naphthalene was used, the mixture was found to be fluid at normal temperatures, whereas the original pitch was semisolid. The naphthalene combined with the tar with surprising readiness and, upon cooling, no traces of the naphthalene could be seen in the resulting mixture, except where high percentages were added. It was found, however, that between 15 and 20 per cent of naphthalene caused the tar to become saturated. The 15 per cent mixture was homogeneous when cold, but in the 20 per cent mixture a small amount of naphthalene crystals separated out upon cooling. This fact indicates that the tar pitch forms a sort of eutectic with naphthalene similar to certain metallic alloys. Above the approximate eutectic of 20 per cent the

naphthalene crystallized out more and more as the percentage was increased. A mixture of 30 per cent of naphthalene solidified. This was due to the crystallization of the excess of naphthalene. The consistency of this mixture at 55° C. was found to be higher than the preceding mixtures, owing to the separation of the naphthalene, which does not melt at this temperature. At 80° C. the consistency

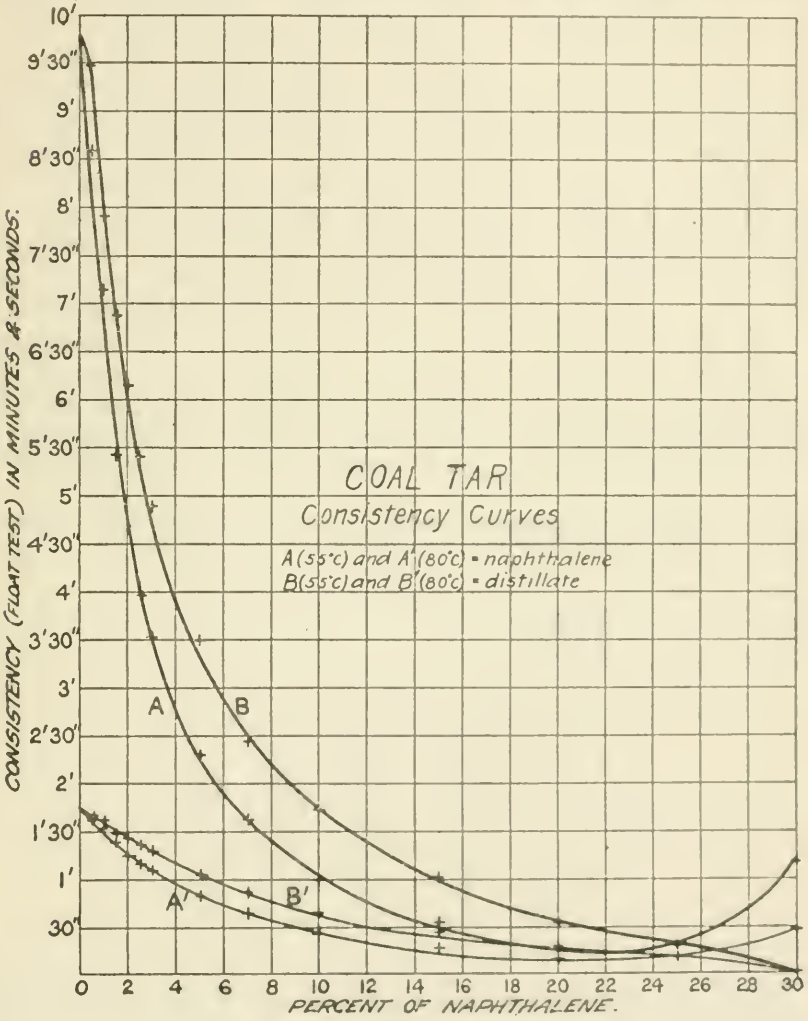

FIG. 1.

of this mixture was nil; that is, it became very fluid, as would naturally be expected. The maximum increase of fluidity of the tar was obtained with 20 per cent of naphthalene, which is practically the eutectic point. These facts will be noticed on the curves A and A′ (fig. 1), which show the consistency of the mixtures plotted against the varying percentages of naphthalene.

Curve A shows the decided effect which naphthalene has upon the tar at 55° C., and A′ the effect at 80° C. As the temperature of the water bath during the float test is raised, the curve A will approach A′ and a series of curves might be obtained, lying between A and A′, for water-bath temperatures between 55° C. and 80° C.

The sensitiveness of the tar pitch to small increments of naphthalene is shown by the sharp drop in the first section of curve A, starting with the addition of 0.5 per cent of naphthalene, which increases the fluidity 1 minute 12 seconds. The fluidity increases very markedly until 7 per cent of naphthalene is reached, when the curve becomes more gradual, while increasing percentages of naphthalene have a much smaller effect. The curve drops, however, until 20 per cent of naphthalene is reached and then rises gradually to 25 per cent of naphthalene, owing to the separation of naphthalene, as previously explained. At 30 per cent of naphthalene a sharp rise is noted and the curve, if continued further, would rise almost perpendicularly, because the naphthalene is so much in excess that an accurate measurement of the consistency would be impossible. For reference to the percentage increase in fluidity owing to increasing increments of naphthalene, the data given in Table I calculated from the curves will show statistically what the curves represent graphically.

TABLE I.—*Percentage increase in fluidity of coal-tar pitch owing to additions of naphthalene and naphthalene-free tar distillate.*

Per cent of naphthalene or distillate.	Due to naphthalene.		Due to distillate.	
	At 55° C.	At 80° C.	At 55° C.	At 80° C.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
0.5	12.2	6.7	3.1	3.8
1.0	26.9	11.5	19.1	5.8
1.5	44.5	19.2	29.6	14.4
2.0	50.8	27.9	37.1	17.3
2.5	59.3	32.7	44.6	20.2
3.0	64.1	36.5	49.9	25.0
5.0	76.5	51.0	64.2	39.4
7.0	83.3	63.5	75.1	49.0
10.0	91.5	75.0	82.3	61.5
15.0	94.4	83.7	89.6	74.0
20.0	97.3	90.4	94.5	83.7
25.0	96.9	89.4	96.6	89.4
30.0	88.1	75.0	100.0	100.0

It will be observed that 7 per cent of naphthalene increases the fluidity of the tar 83.3 per cent at 55° C., while 20 per cent increases it 97.3 per cent, showing that the additional 13 per cent of naphthalene makes an increase of only 14 per cent in fluidity. This fact is shown by the gradual slope of the curve A between these points as contrasted with the steep slope up to 7 per cent.

For comparison with the consistency results obtained with naphthalene, a portion of the original coal-tar pitch was saved for

use in mixtures with a naphthalene-free tar distillate. Duplicate tests were carried out in the same way as were the naphthalene tests, except that equivalent percentages of a naphthalene-free distillate were employed. This distillate was a mixture of oils taken from the distillation of several water-gas tars and showed the following composition upon fractional distillation in an Engler flask:

TABLE II.—*Fractional distillation of tar distillate.*

Temperature in ° C.	Per cent distilled.	Temperature in ° C.	Per cent distilled.
Up to 190	0.7	Up to 280	47.5
Up to 200	1.0	Up to 290	55.5
Up to 210	1.8	Up to 300	62.5
Up to 220	5.0	Up to 310	71.0
Up to 230	7.5	Up to 320	77.5
Up to 240	14.5	Up to 330	83.0
Up to 250	23.0	Up to 340	89.0
Up to 260	28.5	Up to 346[1]	94.0
Up to 270	37.0		

[1] Dry.

The specific gravity of this distillate was 1.006 at 25° C. and, upon cooling to −10° C., no solids crystallized out of solution.

Thirteen samples were weighed out in the same manner as for the naphthalene tests and the percentages of distillate added as before. Consistency results were obtained upon the mixtures of tar and distillate, according to the float apparatus, and at the same temperatures as in the naphthalene tests—55° C. and 80° C. The procedure was exactly duplicated in both cases, so that the results could be studied under exactly the same conditions. In figure 1 the results of this second series of tests are shown by curves B and B′, and the corresponding tabulated data are shown in Table I as compared with the results from naphthalene.

The effect exerted by naphthalene upon the fluidity of tar is, from these results, a very important one in coal tars used for road construction. All coal tars contain naphthalene, but the amount in road-tar preparations varies from 0 to 10 per cent and higher. The degree of fluidity which a tar maintains under service conditions is a most important consideration. The fact that a tar is originally of proper consistency for certain work is no reason for supposing that this consistency will be maintained under service conditions. If the fluidity of the tar is due principally to nonvolatile tar oils, it will undoubtedly maintain its original consistency for a longer period than if the fluidity is due mainly to high naphthalene content. Therefore, in two tars of the same consistency or degree of fluidity, one with a small naphthalene content and the other with a high naphthalene content, it would be natural to predict from the foregoing data that upon exposure the low naphthalene tar would main

tain its original consistency for a longer time, if other things are equal. Owing to the volatility of naphthalene, the high naphthalene tar would undoubtedly lose more or less naphthalene, and hence its fluidity might be expected to decrease rapidly. This subject is now under investigation and will be covered in a later paper.

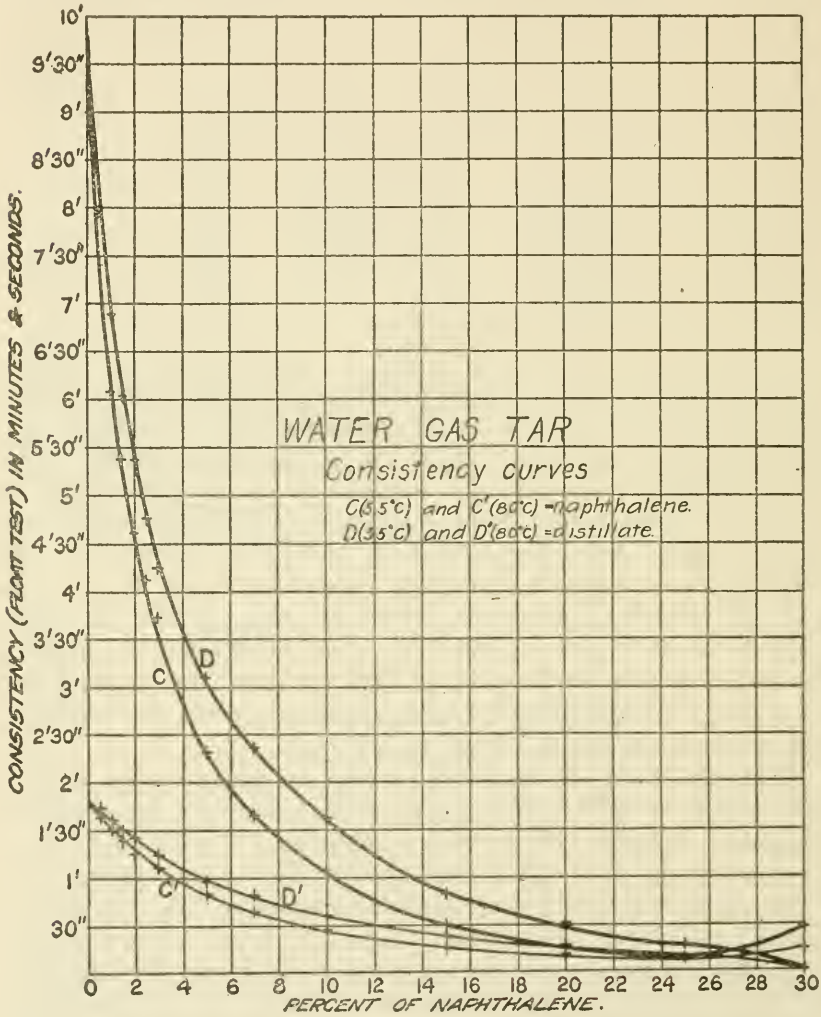

FIG. 2.

In addition to refined coal tars, refined water-gas tars and also refined mixtures of coal tar and water-gas tar are used to a considerable extent in the treatment and construction of roads. For this reason it was thought advisable to determine what effect naphthalene might have upon the consistency of a water-gas tar pitch. Water-gas tar as produced in the modern manufacture of carburetted water

gas is similar in many ways to its sister product, coal tar. It has, however, marked characteristics in which it differs from coal tar, namely, a lower specific gravity, a lower free-carbon content, and a relatively small amount of naphthalene.

A representative sample of water-gas tar was distilled until the residual pitch had as nearly as possible the same consistency at 55° C. as the coal-tar pitch in the previous experiments. This water-tar pitch had a consistency of 9 minutes 49 seconds. It was divided into two portions, one for naphthalene mixtures and one for distillate mixtures. As in the previous work, samples were weighed out with varying percentages of naphthalene and a duplicate set of samples with an equivalent amount of the same naphthalene-free tar distillate as used in the coal-tar tests. The consistency was obtained in both sets of tests with the float apparatus, and the water bath was maintained at 55° C. and 80° C., respectively. The results from the naphthalene series are shown in figure 2 by curves C and C′, and those of the corresponding distillate series by curves D and D′.

It will be noted that these curves follow very closely those shown in figure 1 and are of the same general type. The relation between the consistencies obtained with naphthalene and the naphthalene-free distillate is practically the same as for coal tar, and the respective influence of the increase in fluidity is similar, as shown in Table III. Indeed, this similarity is remarkably close when it is realized that the coal-tar pitch contained 18.34 per cent of free carbon, while the water-gas tar pitch contained only 1.77 per cent of free carbon.

TABLE III.—*Percentage of increase in fluidity of water-gas tar pitch, owing to additions of naphthalene and naphthalene-free tar distillate.*

Per cent of naphthalene or distillate.	Due to naphthalene.		Due to distillate.	
	At 55° C.	At 80° C.	At 55° C.	At 80° C.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
0.5	21.1	5.5	18.8	4.6
1.0	38.0	15.6	29.7	11.9
1.5	45.2	22.0	38.5	16.5
2.0	53.0	30.3	45.2	21.1
2.5	57.9	33.0	51.4	26.6
3.0	62.0	38.5	56.7	31.2
5.0	76.4	54.1	68.4	42.8
7.0	83.1	64.2	75.9	55.0
10.0	89.0	75.2	83.5	67.0
15.0	94.9	85.2	91.5	78.9
20.0	97.1	89.9	94.7	86.2
25.0	98.5	92.7	97.1	90.8
30.0	95.2	87.2	100.0	100.0

Comparing these data with those tabulated for the coal-tar tests, it will be noted that the effect of small percentages of naphthalene is even greater for the water-gas tar than for the coal tar of like consistency, and this is also true of the naphthalene-free distillate, although

the effect is not so marked. The principal difference between the two sets of curves at 55° C. is the marked increase in fluidity caused by both naphthalene and distillate when only 0.5 per cent is added, as even as small an addition as this increases the fluidity by 21.1 and 18.8 per cent, respectively. This fact is shown by the sharp drop in both water-gas tar curves at 55° C. The two series of curves obtained at 80° C. are also similar. The effect of increasing amounts of naphthalene, however, is not so markedly shown as in the curves for the test at 55° C.

In a paper by one of the authors,[1] on the effect of free carbon in tars from the standpoint of road treatment it is shown that an increase in the percentage of free carbon to tar bitumen of a given consistency decreases the fluidity of the resulting product. It is evident, therefore, that the true bitumen of the two tar pitches under investigation, excluding free carbon, differed somewhat, although the pitches as prepared were of the same consistency.

While at the present time it does not seem advisable to draw very definite conclusions, the foregoing results nevertheless strongly indicate the following facts:

(1) That the fluxing value of naphthalene for tar pitches is somewhat greater, although quite similar, to the heavier naphthalene-free tar distillates, until the mixture becomes saturated with naphthalene;

(2) That for the harder tar pitches the addition of very small percentages of naphthalene will produce a marked increase in fluidity of the resulting product;

(3) That for the softer pitches the addition of naphthalene in small quantities causes less increase in fluidity than for the harder pitches;

(4) That where naphthalene is added beyond the point of saturation a rapid decrease in the fluidity of tars at temperatures below the melting point of naphthalene is observed, but at temperatures above its melting point the fluidity continues to increase.

In conclusion, it may be stated that evidence points to the fact that, within a reasonable degree of accuracy, it should be possible to foretell, by reference to the curves which have been given, what consistency to expect from the addition of a given percentage of naphthalene to a tar pitch or refined tar of known consistency, irrespective of the free carbon content of the tar.

[1] Proc. Am. Soc. Test. Mat., 1909, Vol. IX, p. 549.

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